



Consommation et  
Affaires commerciales Canada  
Bureau des brevets  
Ottawa, Canada  
K1A 0C9

Consumer and  
Corporate Affairs Canada  
Patent Office

(21) (A1) 2,088,427  
(22) 1993/01/29  
(43) 1993/08/04

5,049,872

(51) INTL.CL. <sup>5</sup> C08K-007/04; C08L-021/00

(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Vulcanizable Rubber Compositions with Excellent  
Processibility, Good Heat Resistance and Good Mechanical  
and Dynamic Properties

(72) Szentivanyi, Zsolt - Japan ;  
Mezger, Martin - Germany (Federal Republic of) ;  
Igarashi, Nobuo - Japan ;  
Fukuda, Koji - Japan ;  
Nakamura, Atsushi - Japan ;

(73) Bayer Aktiengesellschaft - Germany (Federal Republic of)  
;

(30) (DE) P 42 02 976.7 1992/02/03

(57) 4 Claims

Notice: This application is as filed and may therefore contain an  
incomplete specification.

Canada

CCA 3254 (10-92) 41 7530-21-936-3254

Vulcanizable rubber compositions with excellent processibility, good heat resistance and good mechanical and dynamic properties

---

A b s t r a c t

Vulcanizable rubber compositions containing asymmetric needle-shaped fillers with alkaline surfaces are distinguished by outstanding processibility, good heat resistance and good mechanical properties.

Vulcanizable rubber compositions with excellent processibility, good heat resistance and good mechanical and dynamic properties.

---

- 5 This invention relates to vulcanizable rubber compositions containing asymmetric, needle-shaped fillers with alkaline surfaces, and to the use of the rubber compositions for the production of rubber articles such as V-rib belts, toothed belts, extruded sections and moulded articles.
- 10 It is known that rubber compositions to which light coloured reinforcing fillers are added frequently cause problems in processing. There has therefore been no lack of attempts to improve the processibility of such filled rubber compositions without significantly impairing the
- 15 mechanical properties and/or the heat resistance of the rubber compositions. This problem was hitherto not satisfactorily solved.

It has now surprisingly been found that rubber compositions filled with asymmetric, needle-shaped fillers having an alkaline surface have excellent processing properties without the mechanical and dynamic properties or the heat resistance of the rubber compositions being impaired. The mechanical properties and heat resistance have even been

improved by mixing the said fillers with other fillers such as carbon black.

This invention thus relates to vulcanizable rubber compositions containing, based on the quantity of rubber  
5 put into the process, from 5 to 100% by weight, preferably from 20 to 80% by weight, of asymmetric, needle-shaped fillers with alkaline surfaces having a diameter of from 0.05 to 10  $\mu\text{m}$ , preferably from 0.2 to 0.5  $\mu\text{m}$ , and a length/diameter ratio of from 5 to 120, preferably from 20  
10 to 100.

The asymmetric, needle-shaped fillers preferably have alkaline surfaces with a pH >7, most preferably from 7.5 to 11.

15 The needle-shaped fillers used may be, for example, potassium titanium whiskers (e.g. Tofica Y(R) of Otsuko Chem. Co. Ltd., Japan) and/or needle-shaped calcium silicates (Vansil(R) G of Vanderbilt Co., Inc. USA).

20 The asymmetric needle-shaped fillers and the potassium titanate whiskers may also be added to the vulcanizable rubber compositions as mixtures with other, conventional, fillers, such as carbon black, zinc oxide, magnesium oxide, talc or chalk. The quantity of these fillers depends on the desired properties of the rubber articles to be produced and can easily be determined by preliminary  
25 tests. These fillers are usually added in quantities of about 10 to 100 parts by weight, preferably 20 to 80 parts by weight, based on 100 parts by weight of rubber.

Other auxiliary agents may, of course, also be added to the vulcanizable rubber compositions, for example,  
30 plasticizers, resins and stabilizers for obtaining certain

properties in the crude mixture or the vulcanizates. These auxiliary agents are added in the usual quantities; the most suitable quantity can easily be determined by suitable preliminary tests.

- 5 The needle-shaped fillers may be incorporated in known rubbers by mixing in conventional mixing apparatus. The rubbers used may be natural rubbers, nitrile rubbers, hydrogenated nitrile rubbers, ethylene-propylene-diene polymers, isobutylene-isoprene rubbers, butadiene rubbers,
- 10 styrene-butadiene rubbers, chloroprene rubbers, chlorinated polyethylenes, chlorosulphonated polyethylenes, acrylate rubbers and mixtures of the above-mentioned rubbers. These rubbers are known and a summarizing description has been given in Ullmann, Volume 13, 4th
- 15 Edition, 1977, pages 581 et seq.

Vulcanizates may be produced from the rubber compositions according to the invention by the usual methods of vulcanization and used in the form of any conceivable structures (hoses, seals, driving elements such as V-rib belts and toothed belts, friction elements and moulded articles).

Examples

## Components used:

NR: Natural rubber SMR5

5 NR I: Nitrile rubber of Bayer AG, Leverkusen, having an acrylonitrile content of 34% by weight and a Mooney viscosity of 45 (ML 1+4)/100°C

10 HNBR I: Hydrogenation product of a butadiene/acrylo-nitrile copolymer having an acrylonitrile content of 34% by weight and a residual double bond content of 3.8% by weight, and a Mooney viscosity of 70 (ML 1+4)/100°C, of Bayer AG, Leverkusen

15 HNBR II: Hydrogenation product of a butadiene/acrylo-nitrile copolymer having an acrylonitrile content of 34% by weight, a residual double bond content of 6% by weight and a Mooney viscosity of 72 (ML 1+4)/100°C, of Bayer AG, Leverkusen

20 HNBR III: Hydrogenation product of a butadiene/acrylo-nitrile copolymer having an acrylonitrile content of 39% by weight, a residual double bond content of 1% by weight and a Mooney viscosity of 78 (ML 1+4)/100°C, of Bayer AG, Leverkusen

25 Magnesium oxide: (R) Maglite of Merck/USA

Precipitated  
silica: (R)Vulkasil S of Bayer AG, Leverkusen

Potassium  
titanate  
5 whiskers: (R)Tofica Y of Otsuka Chemical Co. Ltd.,  
Japan

Carbon black  
CB N 550: Degussa AG, Wesseling

Ether thioether: (R)Vulkanol OT of Bayer AG, Leverkusen

10 Zinc oxide: (R)zinkoxidativ of Bayer AG, Leverkusen  
ODPA: Bayer AG, Leverkusen  
(Vulkanox OCD)

ZMMBI: Bayer AG, Leverkusen  
(Vulkacit ZMB-2)

15 Styrenised  
diphenylamine: Bayer AG, Leverkusen  
(Vulkanox DDA)

TBBS: Bayer AG, Leverkusen  
(Vulkacit NZ)

TMTD: (R)Vulkacit Thiuram C of Bayer AG,  
20 Leverkusen

CBS: (R)Vulkasit CZ/MG of Bayer AG, Leverkusen

Compounding

The mixture was prepared on rollers at a roller tempera-

ture of 30°C and a friction ratio of 1 to 1.2. The mixing time was about 20 to 30 minutes during which the material heated up to temperatures of from 50 - 70°C.

The quantity of filler used was calculated in each case to 5 produce vulcanizates having approximately the same hardness (Shore A).

The vulcanizable mixtures were used to produce plates measuring 20 x 20 cm under the following vulcanization conditions: 15 - 20 min at 160°C when vulcanization 10 systems containing sulphur were used; 10 minutes at 190°C when peroxide cross-linking systems were used.

S-2 rods conforming to DIN were punched out of the vulcanized plates and tested to determine the mechanical properties.

- 15 The values obtained are shown in the following Tables.  
The figures given for the formulation are parts by weight.

Example 1

	1	2	3	4	5	6	7	8
NR	100	100	-	-	-	-	-	-
NBR I	-	-	100	100	-	-	-	-
HNBR I	-	-	-	-	100	100	100	100
Stearic acid	1	1	1	1	0.75	0.75	0.75	0.75
MgO	-	-	3	3	-	-	-	-
Precipitated silica	40	-	40	-	-	-	-	-
Potassium titanate whiskers**	-	-	-	65	20	40	65	-
Carbon black CB N 550	-	-	-	8	10	10	10	10
Ether thioether*	-	-	-	-	-	5	5	5
ZnO2	-	-	-	-	-	-	-	-
ZnO	3	3	3	3	-	-	-	-
ODPA	1	1	1.5	1.5	-	-	-	-
ZMMBI	-	-	1.0	1.0	1	1	1	1
Styrenised diphenyl-amine	-	-	-	-	1	1	1	1
TBBS	0.8	0.8	0.7	0.7	-	-	-	-
TMD	-	-	3.0	3.0	2	2	2	2
Sulphur	1.5	1.5	0.7	0.7	0.5	0.5	0.5	0.5
CBS	-	-	-	-	0.5	0.5	0.5	0.5

Mooney viscosity of mixture

NR: SMR 5, Mooney viscosity of mixture

NBR I: ACN 34% by wt.; ML (1+4) 100°C = 45;

HNBR I: ACN 34% by wt.; ML (1+4) 100°C = 70;

3.8% residual double bond contents

\* Vulkanol OT (Bayer AG)

\*\* Tofica Y (Otsuka Chemical Co. Itō, Japan)

Example 1

Table 1 (Continued)

NV.	1	2	3	4	5	6	7	8
<u>Elongation at break after hot air ageing</u>								
$(D_t - D_0) / D_0 (\%) \cdot 100$								
1. 100°C 72 h	-30	-14	-	-	-	-	-	-
2. 140°C 72 h	-	-	-46	-19	-1	+3	+10	-13
3. 140°C 336 h	-	-	-	-	-17	-16	-8	-52

Results: 1) In all cases in which needle shaped fillers are used, higher doses are obtained by comparison with light coloured, reinforcing filler and with carbon black and distinctly lower Mooney viscosity with approximately comparable hardness of the vulcanizate.

- 2) The change in elongation at break as a measure of the ageing process is in all cases distinctly less when needle-shaped fillers are used.

	1	2	3	4	5	6	7
Hnbr II	100	100	100	-	100	100	-
Hnbr III	-	-	-	100	-	-	100
Stearic acid	0.75	0.75	0.75	2	2	2	2
ZnO	3	3	3	2	2	2	2
MgO							
Kalium titanate whiskers	75	-	37	75	-	50	25
N 550 carbon black	-	44	22	-	-	-	-
N 762 carbon black					63	21	42
Phthalic acid							
Polyester **	7	7	7	-	-	-	-
ODPA	2	2	2	1	1	1	1
ZMBI	2	2	2	0.4	0.4	0.4	0.4
TAIC*				1.5	1.5	1.5	1.5
Peroxide **				7	7	7	7
Sulphur	0.5	0.5	0.5	-	-	-	-
CBS	0.5	0.5	0.5	-	-	-	-
TMD	2.0	2.0	2.0	-	-	-	-

\* TAIC: triallylisocyanurate of Akzo Company  
 \*\* Peroxide: Bis-(tart.-butylperoxy isopropyl)-benzene, 40%, Akzo Company  
 \*\*\* (R)Ultramoll PP, Bayer AG, Leverkusen

ODPA: octylated diphenylamine  
 ZMBI: zinc salt of 4- and 5-methylmercaptobenzimidazole  
 CBS: benzothiazyl-2-cyclohexylsulphenamide  
 TMD: tetramethyl thiuramic disulphide

1      2      3 (continued)

	1	2	3	4	5	6	7
<hr/>							
Mooney viscosity of mixture							
ML(1+4)100°C (ME)	52	76	62	74	102	85	95
Hardness (Shore A)	69	69	69	73	73	73	73
Strength (kg/cm <sup>2</sup> )							
Elongation (%)	143	309	334	122	263	207	242
Elongation (%)	610	610	603	294	228	281	269
<hr/>							
Elongation at break after hot air ageing							
$(D_2 - D_0) / D_0 \cdot 100 (\%)$							
140°C 72 h	-16	-38	-23	-	-	-	-
140°C 24 h	-5	-17	-12	-	-	-	-
175°C 72 h				0	-25	-11	-15

**Results:** The mixtures containing needle-shaped fillers again show a markedly lower viscosity of the mixture for the same hardness of vulcanizate.

The age resistance of the vulcanizates containing needle-shaped fillers, measured as relative preservation of the elongation at break, is also distinctly better.

Patent Claims

1. Vulcanizable rubber compositions containing, based on the rubber put into the process, from 5 to 100% by weight of asymmetric, needle-shaped fillers with alkaline surfaces having a diameter of from 0.05 to 10  $\mu\text{m}$  and a length/diameter ratio of from 5 to 120.
- 5 2. Vulcanizable rubber compositions according to Claim 1, characterised in that the needle-shaped fillers used are potassium titanate whiskers.
- 10 3. Vulcanizable rubber compositions, characterised in that the needle-shaped fillers have alkaline surfaces with a pH > 7.
4. Use of the rubber compositions according to Claim 1 for the preparation of vulcanizates.

**SUBSTITUTE  
REPLACEMENT**

**SECTION is not Present**

***Cette Section est Absente***